Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.900727

54 (2015) 2223–2227
May

Taylor & Francis
Taylor & Francis Group

Treatment of geothermal water with high fluoride content by electrocoagulation

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Received 16 November 2013; Accepted 17 February 2014

ABSTRACT

The performance of electrocoagulation (EC) process in the treatment of geothermal water with high fluoride content was studied. The effect of applied current density, electrode plate number, electrode plate distance, and the temperature of geothermal water was investigated. The results show that EC can effectively reduce fluoride content to a low level, which can supply sanitary standard for drinking water in China (GB 5749-2006, 2006). With the increase in current density and electrode plate area, the removal efficiency of fluoride in geothermal water was also increased. However, with electrode plate distance increased from 0.5 to 2.0 cm, the fluoride removal efficiency decreased accordingly. The fluoride removal efficiency was improved when geothermal water temperature was increased from 18 to 38℃, while the fluoride removal efficiency changed little with geothermal water temperature from 38 to 62℃.

Keywords: Fluoride; Geothermal water; Electrocoagulation (EC); Aluminum electrode; Flotation

1. Introduction

The geothermal water is a kind of clean energy and water resources, mainly used for heating and bathing. In recent years, a wave of development and utilization of geothermal resources has been set off in North China. However, the fluoride content of geothermal water is very high (3–10 mg/L) in Northern China [1]. Generally, fluoride concentration in drinking water ranging from 0.5 to 0.8 mg/L prevents people from getting dental cavities, but long-term intake of water that contains more than 1.5 mg/L of fluoride may cause bone disease and mottling of the teeth [2]. The highest fluoride level in drinking water set by China Ministry of Health is 1.0 mg/L [3].

Hence, remediation of fluoride content in geothermal water before using becomes necessary. Various treatment technologies, such as precipitation, ion exchange, membrane, adsorption and electrodialysis, have been employed for fluoride removal [4–7].

In recent years, electrocoagulation (EC) methods, having features like relatively more economic and higher treatment efficiency, have been projected to have potential application in water and wastewater treatment [8]. Some treatment stories such as textile, semiconductor, electroplating, and fluoride-containing wastewater. have been examined in the literature [9–11]. It has also proven its good efficiency for

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drinking water defluoridation [12]. EC uses a direct current source between metal electrodes immersed in polluted water. The electrical current causes the dissolution of metal electrodes into wastewater. The metal ions, commonly iron and aluminum, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. In this research, we use aluminum plates as electrodes, the main reactions involved are as follows:

$$Al \longrightarrow Al^{3+} \quad \text{(Anode)} \tag{1}$$

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \tag{2}$$

$$Al(OH)_3 + xF^- \longrightarrow Al(OH)_{3-x}F_x + xOH^- \tag{3}$$

$$2H_2O + 2e \longrightarrow H_2\uparrow + 2OH \quad \text{(Cathode)} \tag{4}$$

Defluoridation is achieved by the forming of $Al(OH)_{3-x}F_x$. At the same time, the fine hydrogen gas bubbles generated at the cathode can enhance F^- mass transfer and float the $Al(OH)_{3-x}F_x$ flocs to the top of the EC reactor. Since fluoride in the water is transferred to $Al(OH)_{3-x}F_x$, the latter must be separated effectively from the water in order to achieve defluoridation effect [13].

In this study, the effects of applied current density, electrode plate area, electrode plate distance, and the temperature of geothermal water on EC performance for the removal of fluoride from high fluoride content geothermal water were investigated in detail.

2. Materials and methods

2.1. Materials

All chemicals used in the experiments were analytical grade or higher and were used as received without further purification (*CH_3COOH, CAS No.: 64-19-7; NaCl, CAS No.: 7,647-14-5; CDTA, CAS No.: 482-54-2; NaOH, CAS No.: 1,310-73-2; CH_3COONa, CAS No.: 127-09-3; NaF, CAS No.: 7,681-49-4*). All solutions were prepared with ultrapure/deionized water. Geothermal water samples were obtained from Daxing district in Beijing, China.

2.2. Analysis

The geothermal water samples were analyzed using the Standard Analysis Methods of China [14]. A selective ion sensor electrode was used to determine the fluoride concentration according to the standard method. To prevent the interference from other ions (Al^{3+}, Fe^{3+}, Cu^{2+}, and Ca^{2+}), TISAB II buffer solution containing CDTA (cyclohexylenediamine tetraacetic acid) was added to the samples. The geothermal water characteristics and drinking water standard of China and (WHO) World Health Organization were presented in Table 1.

2.3. Electrocoagulation procedure

The experimental equipment schematically is shown in Fig. 1. The electrolytic cell was designed as a parallelepipedic plexiglas reactor. The valid working volume, length, width, and height of reactor were 6000 mL, 30, 20, and 15 cm, respectively. An external water jacket for temperature control was equipped surrounding the EC reactor. In all cases, aluminum electrode plates (98.92%; dimensions: 20 × 10 cm; thickness: 1 mm) were used as anode/cathode pair. The cathode and anode electrodes were alternately arranged and placed in the middle of the reactor. The

Table 1
Characteristics of geothermal water

Parameters	Concentration	Chinese drinking water standard [15]	WHO drinking water standard [16]
pH	7.0–7.4	6.5–8.5	/
Temperature	37–49℃	/	/
Fluoride	7.4–9.5 mg/L	1.0 mg/L	1.5 mg/L
Conductivity	0.46–0.52 s/cm	/	/
Fe	<0.3 mg/L	0.5 mg/L	0.3 mg/L
Mn	<0.1 mg/L	0.3 mg/L	0.1 mg/L

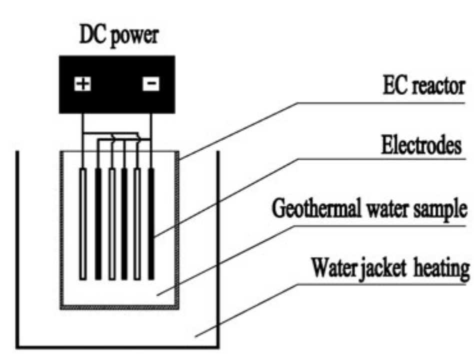

Fig. 1. Diagram of an EC reactor experimental setup.

DC power supply was a MPS 702 DC power generator. Cell potential was controlled by a voltmeter. The geothermal water was analyzed for various parameters according to standard methods of China [14].

3. Results and discussion

3.1. Effect of applied current density

In all electrochemical processes, applied current is the most important parameter for controlling the reaction rate within the electrochemical reactor. The current determines the coagulant dosage rate, the bubble production rate, the growth of flocs, and the fluid regime (mixing) within the reactor [17]. To investigate the effect of electric current on the removal efficiency of fluoride, EC process was carried out using various current density (6.25, 10, 15, and 20 A/m^2) when pH was 7.1 and electrode plate distance was 1.0 cm with 3 pairs of electrode plates. Within 20 EC minutes, the effect of current density on the fluoride removal is shown in Fig. 2.

As shown in Fig. 2, the removal rate of fluoride increased with increasing current, and the highest current density (20 A/cm^2) produced the quickest removal rate. Current density determines the amount of the dissolution of the aluminum electrode. The higher of applied current density, the aluminum fluoride polymers on the same plate area were generated more. However, as the current density increases, the polarization of the electrodes and passivation phenomena was also increased, which influenced the treatment effect. It also resulted in the desired increase in voltage and power loss. So, the current density of 10 A/cm^2 was determined as the optimal current density in our experiment.

3.2. Effect of electrode plate area

Electrode plate area determines the amount of aluminum dissolution and sequentially influences the treatment efficiency in the electrochemical process. EC process was carried out using various electrode plate areas (1, 2, 3, and 4 pairs of plates) when current density was 10 A/cm^2, pH was 7.1 and electrode plate distance was 1.0 cm. Within 20 EC minutes, the fluoride removal is shown in Fig. 3.

It can be seen from Fig. 3 that with increasing of electrode plate areas, the fluoride removal efficiency increased. When the current density is determined, the amount of aluminum dissolution is constant with the same electrode plate area. Therefore, with the increase in electrode plate area, the dissolution of aluminum increased with the aluminum fluoride polymer increasing. Considering of saving electrode material and energy consumption, 3 pairs of plates were selected as the optimal electrode plate areas in the experiment.

3.3. Effect of electrode plate distance

It is known that the distance between electrodes plate not only determines the number of aluminum plates in a given reactor, but also changes the resistance between anode and cathode. What is more, the electrode distance influences on pollutant removal efficiency [18]. EC process was carried out using various electrode plate distance (0.5, 1.0, 1.5, and 2.0 cm) when current density was set at 10 A/cm^2, pH was 7.1 with 3 pairs of electrode plates. Within 20 min, the effect of electrode plate distance on the fluoride removal is shown in Fig. 4.

Fig. 4 illustrates that with increasing of electrode plate distance, the fluoride removal efficiency

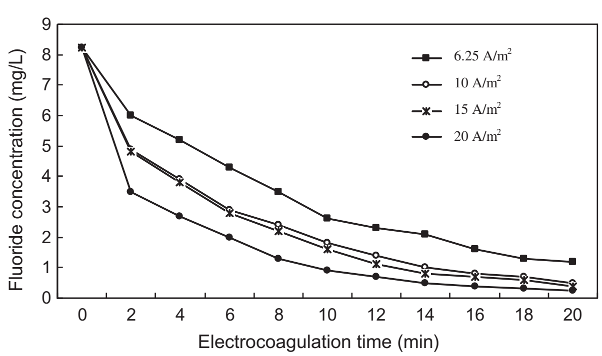

Fig. 2. Fluoride residual concentration as a function of electric current density. (Experimental conditions: pH 7.1; electrode plate distance: 1 cm; 3 pairs of plates.)

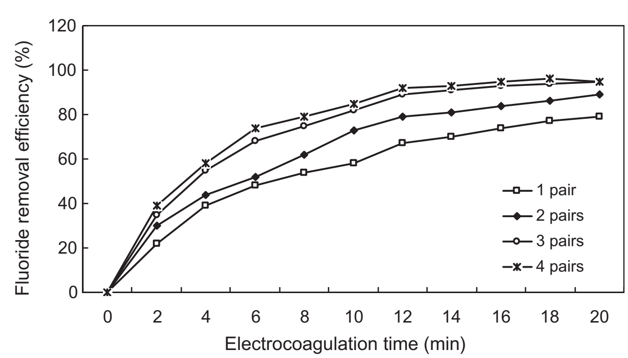

Fig. 3. Fluoride residual concentration as a function of electrode plate areas. (Experimental conditions: initial fluoride concentration: 8.2 mg/L; current density: 10 A/cm^2; pH 7.1; electrode plate distance: 1 cm.)

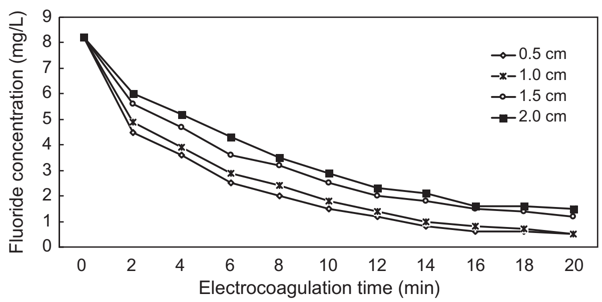

Fig. 4. Fluoride residual concentration as a function of electrode plate distance. (Experimental conditions: current density: 10 A/cm^2; pH 7.1; 3 pairs of plates.)

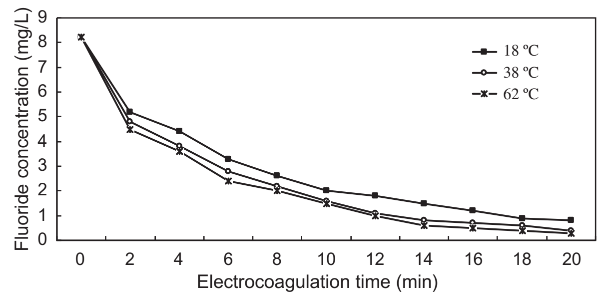

Fig. 5. Fluoride residual concentration as a function of geothermal water temperature. (Experimental conditions: current density: 10 A/cm^2; pH 7.1; electrode plate distance: 0.5 cm; 3 pairs of plates.)

decreased. When the electrode plate distance is short, the bubbles formed by the cathode caused a powerful air flotation effect. As a result, the formed aluminum fluoride polymer was floated up and removed. It also accelerated the further dissolution of the anodic aluminum. However, if the electrode plate distance is too short, the current density will be too high and likely to cause a short circuit. So, the electrode plate distance cannot be further reduced. In our research, the distance of 0.5 cm was selected as the optimal electrode plate distance in our experiment.

3.4. Effect of geothermal water temperature

The effect of temperature on EC process is often neglected in the previous study and will directly affect the removal efficiency [19]. The temperature changed will result in a variation of surface tension phenomena, with probably different hydrodynamic behavior of the suspended matter. In the presence of hydrogen bubble, it will certainly affect the flotation efficiency.

EC process for geothermal water was carried out at different temperatures (18, 38, and 62℃, water jacket heating through electric) when current density was set at 10 A/cm^2, pH was 7.1 and electrode plate distance was 0.5 cm with 3 pairs of electrodes. Within 20 min, the effect of geothermal water temperature on the fluoride removal is shown in Fig. 5.

Fig. 5 shows that the fluoride removal efficiency was improved when geothermal water temperature was increased from 18 to 38℃. However, the fluoride removal efficiency changed little when geothermal water temperature was increased from 38 to 62℃. Therefore, it is not necessary to increase the geothermal temperature for improving the fluoride removal efficiency. Geothermal water can be treated in the original temperature between 37 and 49℃.

3.5. Fluoride removal efficiencies of various treatment processes

The comparison of fluoride removal with different processes was given in Table 2.

Hichour et al. [20] used dialysis process to defluoridate solutions made to simulate high fluoride African groundwater (>30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L. Tripathy et al. [21] investigated the efficacy of alum-impregnated activated alumina in removal of fluoride from water. The

Table 2
Comparison of fluoride removal of various treatment processes

Treatment method	Initial fluoride concentration (mg/L)	Left fluoride concentration after treatment (mg/L)	Operating cost (US $/ton water)	Reference
Dialysis	>30	<1.5	/	[20]
Activated alumina adsorption	25	1.9	/	[21]
Red mud adsorption	21	2.7	0.185	[22]
Layered double hydroxides (LDHs)	50	1.0	0.23	[23]
Electrocoagulation	7.4–9.5	<1.0	0.206	This study

results showed when 25 mg/L fluoride was initially present, the left fluoride in solution was 1.9 mg/L after adsorption. Cengeloglu et al. [22] employed red mud as an adsorbent to defluoridate in water. After adsorption for 2 h at the optimum pH of 5.5, the activated red mud could remove 77% of 21 mg/L fluoride, leaving 2.7 mg/L fluoride in solution. Lv et al. found that the fluoride concentration in water can be reduced from 50 to 1 mg/L with the application of layered double hydroxides [23]. In this study, after 20 min of EC, the fluoride concentration in geothermal water was able to reduce from 7.4–9.5 mg/L to below 1.0 mg/L.

4. Conclusions

The applicability of EC in the treatment of high fluoride content geothermal water was investigated. This electrochemical technique has been applied to produce Al^{3+} with an aluminum anode. The experimental results showed that with increasing of applied current density and electrode plate area, the removal efficiencies of fluoride increased accordingly. With increasing of electrode plate distance from 0.5 to 2.0 cm, the fluoride removal efficiency decreased. As for geothermal water temperature, the fluoride removal efficiency was improved when geothermal water temperature was increased from 18 to 38℃, and the fluoride removal efficiency changed little when geothermal water temperature was increased from 38 to 62℃.

Acknowledgments

We gratefully acknowledge the financial support provided by the China Central University Special Basic Research Fund (No. 2011QH01).

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